Experimental evidence of perturbed odd hydrogen and chlorine chemistry after the October 2003 solar proton events

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[1] Time series of stratospheric ClO and HOCl have been measured with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on board the Environmental Satellite (ENVISAT) during the solar storm episode in October/November 2003. A remarkable enhancement of ClO mean values (averaged over latitudes poleward from 70°N) was found, reaching values of more than 0.2 ppbv and even 0.4 ppbv when only nighttime measurements are considered. HOCl was found to increase by up to more than 0.3 ppbv at altitudes above 32 km. This gives indirect proof of enhanced odd hydrogen abundances as a consequence of the solar proton events between 27 and 31 October 2003. Simultaneous increase of both ClO and HOCl hints at HCl destruction either through OH or directly via ion cluster chemistry. When HOCl and ClO mixing ratios decreased, most probably due to then lowered odd hydrogen abundances, large amounts of $ClONO_2$ (polar cap averages enhanced by up to 0.4 ppbv) in early November indicate that ClO then was buffered in this reservoir. Daytime Antarctic ClO enhancements reach 0.2 ppbv and are largest above approximately 40 km. The largest response of Antarctic nighttime ClO is seen at 35 km altitude, where the enhancement reaches 0.3 ppbv. HOCl enhancement in the southern stratosphere was weaker by approximately a factor of two compared with the northern counterpart. The most prominent HOCl increase in the southern stratosphere was observed in subpolar regions between 60°S and 70°S.

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1. Introduction

[2] The solar storm in October–November 2003 caused major solar proton events (SPEs) on 29 and 31 October as well as 3 and 5 November (http://sec.noaa.gov/Data/goes.html). Highly energetic particles of energies between 30 and 100 MeV reached the Earth and penetrated into the middle atmosphere. This led to increased ionization of the upper stratosphere and mesosphere, which, according to model calculations by *Krivolutsky et al.* [2005] reached its maximum at 0900 UT on 29 October at 60 km altitude. This caused generation of large amounts of NO_x (N + N(excited) + NO + NO_2) and NO_y [*López-Puertas et al.*, 2005a, 2005b; *Seppälä et al.*, 2004; *Orsolini et al.*, 2005] which were measured with the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS). Subsequent ozone destruction, also measured by MIPAS, is only partly attributed to NO_x chemistry. In particular in the upper stratosphere and lower mesosphere, odd hydrogen (HO_x = H + OH + HO_2), which is formed as described by *Solomon et al.* [1981], is supposed to be a major ozone depletion path [*Jackman and McPeters*, 2004; *Jackman et al.*, 1995; *Degenstein et al.*, 2005; *Krivolutsky et al.*, 2005, and references therein]. In particular, the immediate short-term ozone loss found by *López-Puertas et al.* [2005a] suggests a dominant role of HO_x chemistry there, which is characterized by much shorter timescales. Unfortunately, odd hydrogen species have not been measured during a solar proton event directly. However, enhanced odd hydrogen resolves atomic chlorine from the reservoir HCl via the reaction

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(R2) $\quad OH + HCl \rightarrow H_2O + Cl.$

Since the reaction

$$\text{(R3)} \qquad Cl + O_3 \rightarrow ClO + O_2$$

is very fast, enhancement of ClO indirectly hints at increased odd hydrogen abundances unless other plausible ClO sources are found, such as ion cluster chemistry which might directly decompose HCl, immediately followed by R3.

[3] Further, enhanced odd hydrogen gives raise to high HOCl values via the reaction

$$\text{(R1)} \qquad ClO + HO_2 \rightarrow HOCl + O_2.$$

Therefore both ClO and HOCl measurements, as both available from MIPAS, can be used as indicators for enhanced HO_x abundances. HO_x chemistry is also linked to NO_x and NO_y chemistry via the formation of HNO_3, which is discussed in companion papers by *López-Puertas et al.* [2005a, 2005b].

2. Michelson Interferometer for Passive Atmospheric Sounding

[4] MIPAS on board the Environmental Satellite (ENVISAT), which was launched into its Sun-synchronous polar orbit on 1 March 2002, is a limb emission Fourier transform spectrometer designed for measurement of trace species from space [*European Space Agency*, 2000; *Endemann and Fischer*, 1993; *Endemann et al.*, 1996; *Fischer and Oelhaf*, 1996]. Its high spectral resolution of 0.05 cm^{-1} in terms of full width at half maximum (apodized with the "strong" *Norton and Beer* [1976] function) allows measurement of many species, in particular of minor constituents of the Earth's atmosphere. Since MIPAS is a limb emission instrument, measurements are possible on the dayside and the nightside of the Earth, and polar regions are covered also during polar night conditions. Data presented here are IMK-version V2_HOCl_1 and V2_ClO_1 and were recorded between 21 October 2003 and 14 November 2003. Data from 28 October are missing since MIPAS was switched off during this day.

3. Retrieval of Vertical Profiles

3.1. Retrieval of ClO

[5] The retrieval of ClO profiles used in this study was performed as documented by *Glatthor et al.* [2004]. The P and Q-branch transitions of the 1–0 band between 820.975 and 846.175 cm^{-1} were used for the retrieval. Under polar winter conditions, useful data can be retrieved in the lower stratosphere up to about 22 km altitude. Single profile retrieval errors are estimated at approximately 0.6 ppbv (30%) at the peak altitude (typically around 18–20 km), at an altitude resolution of approximately 4 km. The error budget is dominated by noise and spectroscopic data uncertainties, with error contributions of comparable importance. In the case of perturbed atmospheres, the altitude range where useful data can be obtained is extended to about 50 km, which allows assessment of the ClO upper maximum. The altitude resolution, however, exceeds 10 km and single profile random noise is 30–50% there.

3.2. Retrieval of HOCl

[6] The retrieval of HOCl profiles presented in this paper was performed as described by T. von Clarmann et al.

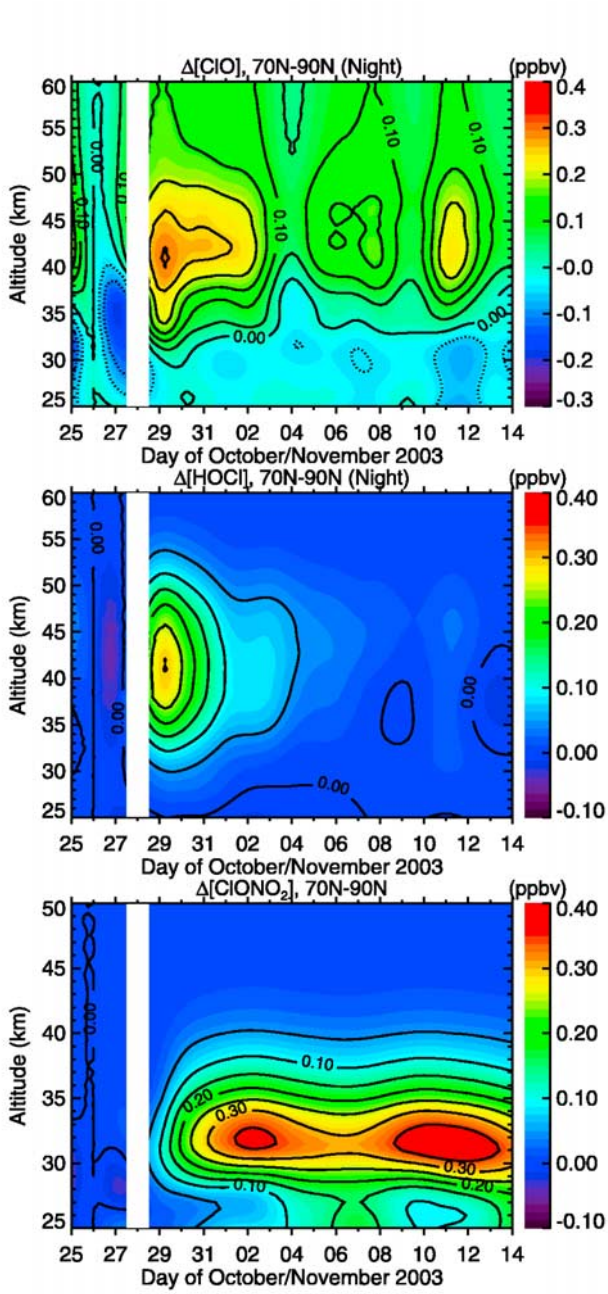

Figure 1. Temporal development of northern polar (top) ClO, (middle) HOCl, and (bottom) $ClONO_2$ enhancements between 70 and 90°N between 25 October and 14 November 2003, related to background conditions measured on 26 October. The 48-hour polar cap averages have been weighted by the cosine of latitude in order to account for the different area represented by each data point. The large averaging interval has been chosen to remove sampling artefacts. Only nighttime spectra were considered for representation, not primarily because of diurnal effects but because Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) has observed the areas of largest enhancement during nighttime and inclusion of daytime measurements would partly mask the effect. The white band on 28 October represents a data gap when MIPAS was switched off.

Figure 1 (top) for all relevant altitudes, and in Figure 2 (top) as a time series at 40 km altitude, both at a time resolution of 48 hours (triangular filter with 48 hours full width at half maximum, on a 24-hour sampling grid). In order to account for the different area represented by each MIPAS data point, measured mixing ratios have been weighted by the cosine of the latitude for averaging.

[9] Until 28 October 2003, no significant ClO amounts were detected in the northern polar stratosphere between 70°N and 90°N at about 40 km altitude. Immediately after the first major SPE, MIPAS ClO measurements show a rapid enhancement at altitudes above 30 km, with maximum values of more than 0.3 ppbv at 42 km. Since no other rapid and efficient source for chlorine atoms was evident, the ClO increase is attributed to HCl decomposition, either by ion cluster chemistry or by increased odd hydrogen abundances immediately after the solar storm. In the latter case, R2 releases Cl from HCl. Atomic chlorine then rapidly is converted to ClO according to R3. While unfortunately HCl is not measured by MIPAS, the rapid ClO formation most probably is an indicator for increased odd hydrogen abundances. The maximum ClO mixing ratios were reached within one day after the most pronounced SPE on 29 October (see *López-Puertas et al.* [2005a, Figure 1] for temporal development of solar proton fluxes), which hints at an immediate response of odd hydrogen chemistry to the SPE. The "shoulder" in the time series around day 5 in Figure 2 (top) could be a response to the second large SPE on 30 October.

[10] The HOCl response to the first major SPE is very similar compared with ClO both in terms of amplitude (0.3 ppbv) and temporal development (Figure 1, middle and top, and Figure 2). Until 28 October 2003, the normal background mixing ratios of 0.1–0.2 ppbv were detected in the northern polar stratosphere. On 29 October, a rapid increase of HOCl mixing ratios was observed at altitudes from 32 km to 50 km. The largest increase was observed at 41 and 42 km altitude, where an enhancement of 0.3 ppbv relative to pre-SPE conditions (25 October) was measured. While the maximum of OH increase is expected at altitudes between 65 and 80 km [*Jackman et al.*, 2005; *Krivolutsky et al.*, 2005], limited availability of ClO shifts the maximum of the HOCl response to lower altitudes. As for ClO, also the HOCl maximum mixing ratios were reached within 1 day after the most pronounced SPE on 29 October, which again hints at an immediate response of odd hydrogen chemistry to the SPE. Thus the time lag of 48 hours between the SPE and the OH maximum as postulated by *Krivolutsky et al.* [2005] is not confirmed by MIPAS measurements, where ClO and HOCl mixing ratios already started to decline on 29 October. The apparent HOCl enhancement before the 29 October SPE in fact is an artefact in the representation caused by interpolation over the data gap on 28 October. This rapid enhancement of the area-weighted polar cap HOCl mean values is followed by a decline with a half value period of approximately 0.8 days (Figures 1 and 2). This exceeds typical lifetimes of SPE-induced HO_x, which are estimated at several hours in the middle atmosphere by *Jackman et al.* [2005]. This short-term memory effect implies that the extended existence of enhanced HOCl gives no evidence that OH abundances are still enhanced.

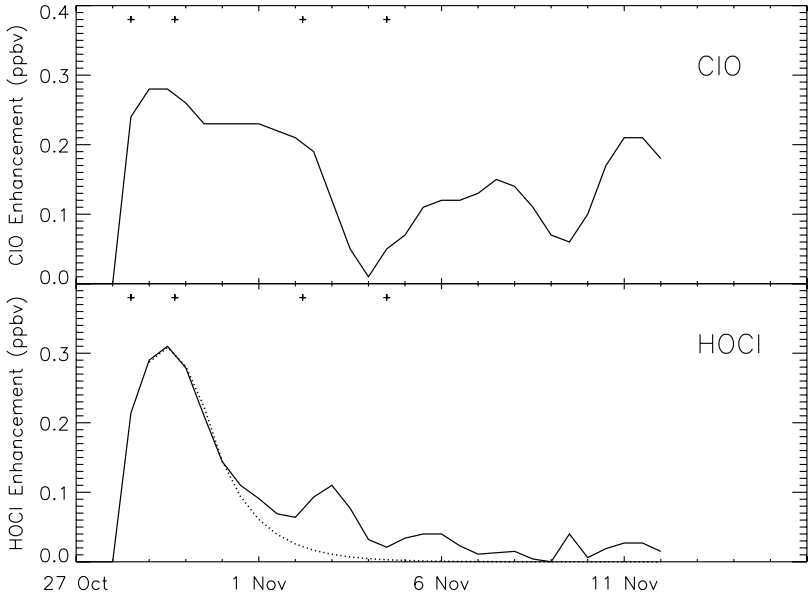

Figure 2. Time series of northern polar mean nighttime (top) ClO and (bottom) HOCl enhancements between 70 and 90°N between 25 October and 14 November at 40 km altitude. The dotted line in the lower panel describes an ideal exponential HOCl decrease with a half value period of 0.8 days from the maximum value, convolved with a triangular filter function of 48 hours full width at half maximum for reasons of comparability to observed data. Crosses indicate commencements of high energetic solar energetic particles.

[11] Since HOCl is part of a catalytic cycle

$$(R1') \qquad ClO + HO_2 \rightarrow HOCl + O_2$$

$$(R4) \qquad HOCl + h\nu \rightarrow OH + Cl$$

$$(R3') \qquad Cl + O_3 \rightarrow ClO + O_2$$

$$(R5) \qquad OH + O_3 \rightarrow HO_2 + O_2$$

$$(R6) \qquad \text{Net: } 2O_3 \rightarrow 3O_2,$$

and since there are also nonphotochemical loss reactions, of which

$$(R7) \qquad HOCl + OH \rightarrow H_2O + ClO,$$

is the most efficient one in the absence of atomic oxygen, high abundances can only be maintained with enough HO_2 and ClO available. The HOCl response to the second large SPE on 30 October is not distinguishable in Figure 1 (top) and Figure 2. Since the temporal evolution of HOCl shown in these figures is based on 48-hours averaging, this HOCl enhancement cannot be well resolved. The short-term temporal development is well explained by the exponential decrease, which one expects as typical reduction function relative to sharp termination of HOCl formation.

[12] No pronounced ClO response to the subsequent SPE on 2–3 November, when high-energetic proton flux was measured for a much shorter time, is observed; only a weak HOCl response to this SPE is visible in Figures 1 and 2, which is much less pronounced than that to the 29 October SPE. Calculations of SPE-induced odd hydrogen production as performed by *Jackman et al.* [2005] for Antarctic conditions show only a very weak HO_x enhancement for this date, due to low ionization at these altitudes. Similar temporal evolution of HO_x in the Arctic stratosphere would directly explain the weak HOCl response to the November SPEs.

[13] Some minor apparent ClO and (to a lesser extent) HOCl enhancements are visible on 8 and 11 November, which do not seem to be produced by SPEs (Figures 1 and 2). On these days only enhancement of solar lower-energy proton fluxes (below 10 MeV) was observed, which typically do not penetrate into the stratosphere. However, the November enhancements should not be overstressed: first, because within the timescale of several days after the first SPE, superposition of transport and subsidence effects makes it difficult to unambiguously assign a signal in the time series to a single origin; also, for several days during this period only very few MIPAS data are available and the apparent ClO and HOCl responses might be pure sampling artefacts.

[14] Analysis of the temporal development of $ClONO_2$ reveals a strong increase of this reservoir species from 30 October to 2 November [see also *López-Puertas et al.*, 2005b], in particular at altitudes below 40 km, with a maximum amplitude at 32 km (Figure 1 (bottom); see also Figure 3, third row). This indicates that active chlorine was buffered into its inactive reservoir there and is consistent with decreasing ClO and HOCl abundances. This suggests that in the middle stratosphere, SPE-induced enhanced odd hydrogen abundances have perturbed the partitioning of chlorine reservoirs toward $ClONO_2$ through R2 and R3 and

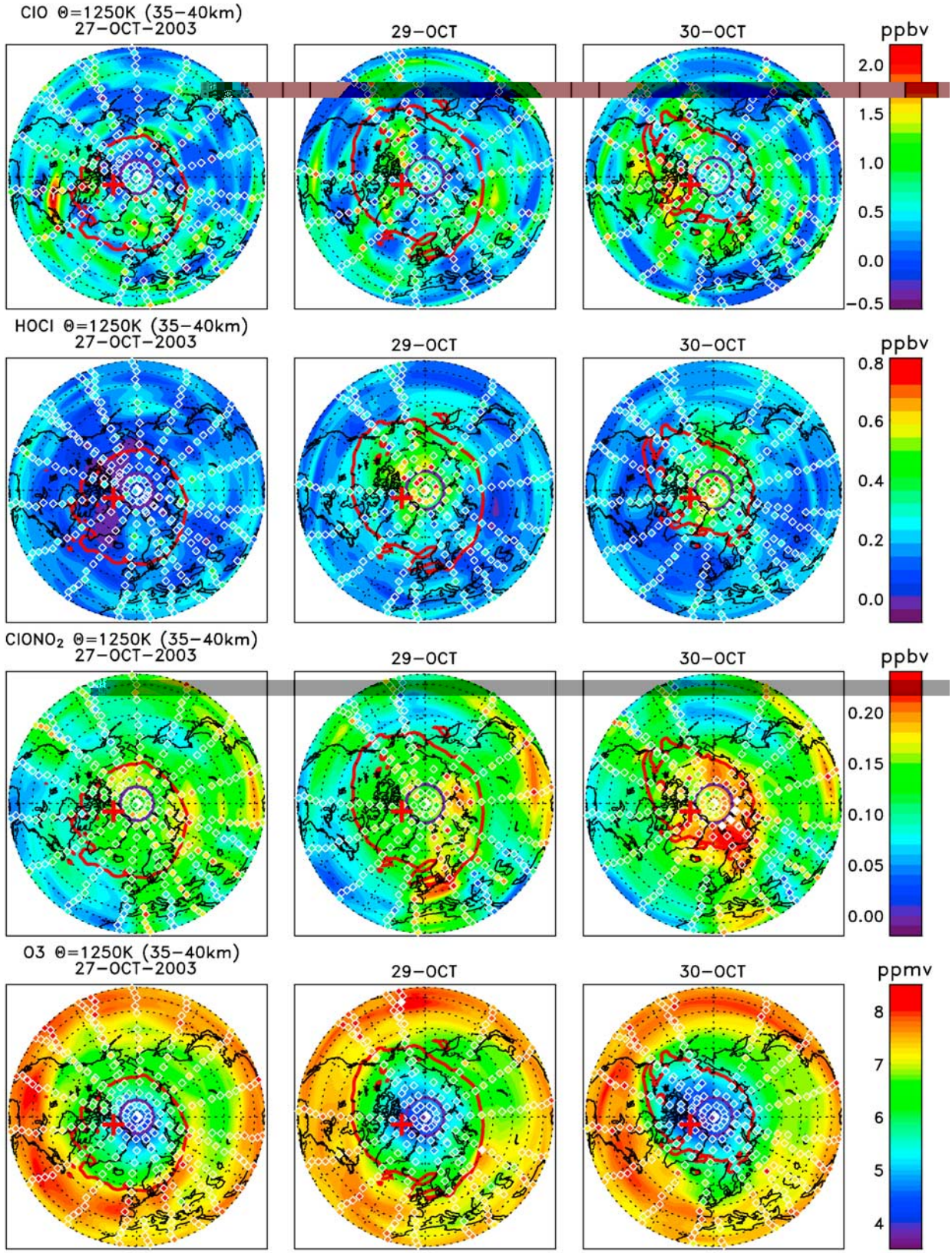
ClO Θ=1250K (35–40km)
27–OCT–2003
29–OCT
30–OCT
ppbv
2.0
1.5
1.0
0.5
0.0
−0.5
HOCl Θ=1250K (35–40km)
27–OCT–2003
29–OCT
30–OCT
ppbv
0.8
0.6
0.4
0.2
0.0
ClONO2 Θ=1250K (35–40km)
27–OCT–2003
29–OCT
30–OCT
ppbv
0.20
0.15
0.10
0.05
0.00
O3 Θ=1250K (35–40km)
27–OCT–2003
29–OCT
30–OCT
ppmv
8
7
6
5
4

Figure 3

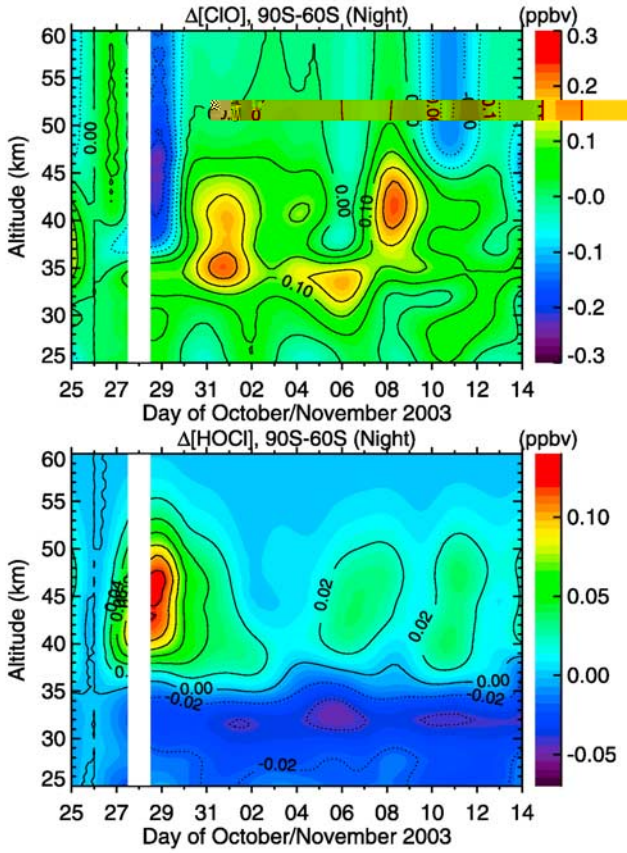

Figure 4. Temporal development of southern polar nighttime (top) ClO and (bottom) HOCl. Same representation as for Figure 1, except that latitudes between 60°S and 90°S have been considered.

subsequent $ClONO_2$ formation. The low altitude of maximum $ClONO_2$ response just reflects the pressure dependence of $ClONO_2$ formation from ClO and NO_2. The larger amplitude of the $ClONO_2$ signal compared with the combined HOCl and ClO signal is explained by the fact that at lower altitudes a substantial part of ClO during nighttime forms the ClOOCl dimer and thus is not visible for MIPAS. At typical temperatures of about 205 K and below 32 km in the air masses sounded by MIPAS, up to 50% of the ClO molecules are estimated to be trapped in the dimer. With this assumption, [ClO] + [HOCl] + 2[ClOOCl] + [$ClONO_2$] stays approximately constant during the process of $ClONO_2$ formation at 32 km. At higher altitudes, excess chlorine apparently forms again HCl after the perturbation phase.

[15] On 29 October the area of largest HOCl enhancement is not centered at the geographic pole but, as expected, shifted slightly toward the higher geomagnetic latitudes (Figure 3, second row). On the following days, areas of large HOCl mixing ratios were smaller but still characterized by values as large as during the preceding days. However, large HOCl abundances were then found in a region centered around the geographic pole, where, owing to polar winter conditions, the atmosphere was always dark. Here neither HOCl photolysis (R4) nor decomposition according to reaction R7 was possible, which explains the longer HOCl lifetime, contrary to lower latitudes, where existing HOCl was photolyzed (R4) or decomposed via reaction R7 during part of the day. Since due to its short lifetime no excessive HO_2 was available then, no substantial HOCl amounts could be produced. This evidently led to a shift of the equilibrium abundance to lower values there. On 30 October the small area of enhanced HOCl was surrounded by a band of high $ClONO_2$, which was complemented by ClO at regions, where $ClONO_2$ still was low, i.e., from Baffin Bay to Beaufort Sea (Figure 3, first and third rows). The spatial anticorrelation between ClO and $ClONO_2$ indicates a longitudinal, nitrogen chemistry, and/or diurnal dependence of Cl reservoir formation. While there is large scatter in measured ClO data, there appears to be some spatial anticorrelation also between ClO and HOCl. Low HOCl mixing ratios where ClO was high suggest that the lack of ClO through buffering of active chlorine into its reservoir $ClONO_2$ may not have been a major obstacle to HOCl formation (R1) in the later phase of the SPE period. Otherwise, one would expect enhanced HOCl values at least where ClO was still available. $ClONO_2$ formation seems rather to be amplified by release of ClO through R4 followed by R3 and R7 in the sunlit atmosphere than to be the cause of reduced HOCl, which appears to be primarily driven by odd hydrogen chemistry.

[16] The maximum ozone destruction signal in the polar atmosphere between 70° and 90° around 65 km is attributed to odd hydrogen chemistry and precedes the maximum NO_x enhancement there [c.f. *López-Puertas et al.*, 2005a, Figure 3]. Unfortunately, at these high altitudes, no HO_x species have been detected with MIPAS so far; also HOCl is below the detection limit there. A pronounced second maximum of ozone depletion at about 40–50 km altitude appears immediately after the SPEs on 29 October. While low ozone (below 5 ppmv at 40 km) had already been observed before, in particular in a small unilluminated area over the North Pole, averaged mixing ratios are reduced by 30% at 40–50 km altitude thereafter, owing to the extension of the low ozone area. No such ozone loss maximum at 42 km is predicted by model calculations by *Krivolutsky et al.* [2005]. NO_x induced ozone loss can be ruled out here since ozone decrease after 29 October appears to be much faster than the NO_x increase found by *López-Puertas et al.* [2005a], suggesting that either HO_x or HOCl or ClO chemistry could noticeably have contributed to the early O_3 response to the SPE. This is in agreement with the established theory that the NO_x cycle

Figure 3. Arctic ClO, HOCl, $ClONO_2$, and ozone distributions as measured by MIPAS on 27, 29, and 30 October 2003 at a potential temperature level of 1250 K, corresponding to approximately 35 to 40 km altitude. The diamonds represent the MIPAS measurements, while the background color and contours represent values zonally smoothed within 700 km, whereby each measurement was weighted by the cosine of latitude in order to account for the different area it represents. The geomagnetic pole is represented by a red cross. The boundary of the polar vortex is indicated by the red line. The vortex boundary was determined using the criterion proposed by *Nash et al.* [1996], modified such that CH_4 was used as vortex tracer instead of zonal winds. The black circle represents the terminator.

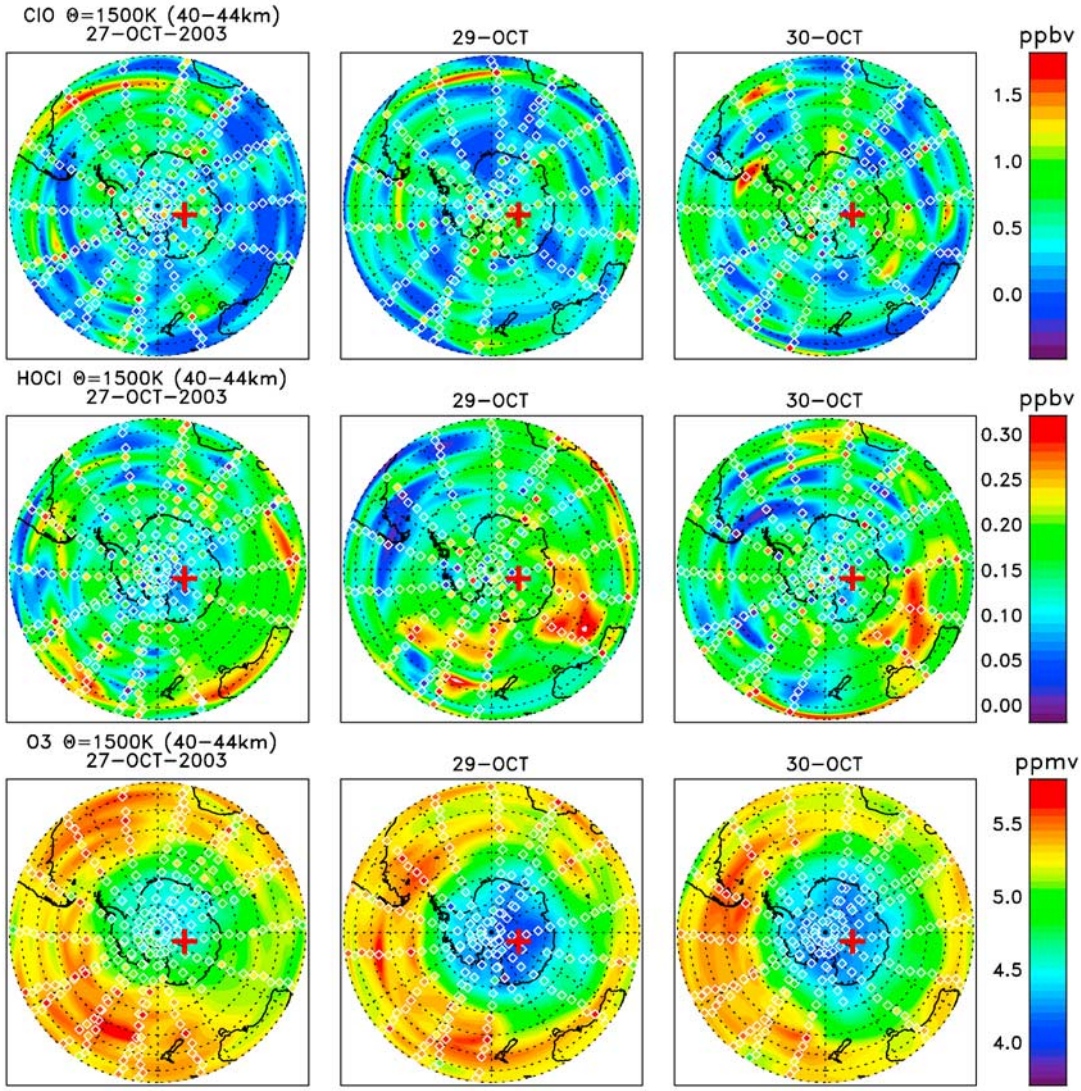

Figure 5. Antarctic ClO, HOCl, and O_3 distributions as measured by MIPAS on 27, 29, and 30 October 2003 at a potential temperature level of 1500 K, corresponding to approximately 40 to 44 km altitude. The red cross represents the geomagnetic pole. No intact vortex was found at these altitudes.

plays a minor role in ozone destruction at these altitudes [*Lary*, 1997]. Uncertainties in HOCl formation reaction constants [*Kovalenko et al.*, 2004; *Salawitch et al.*, 2004] cause uncertainties in related model calculations and thus make it difficult to quantitatively predict the role of HOCl chemistry itself in SPE-induced ozone reduction. Poor spatial anticorrelation of HOCl and O_3 at least suggests that HOCl chemistry is not the major ozone depleting mechanism (Figure 3, lowermost row). On the other hand, the region of lowest ozone is not centered over the pole but shifted toward the region of highest ClO. This suggests enhanced chlorine-induced ozone destruction in the stratosphere as a further consequence of the solar storm, which is superimposed to the NO_x-induced ozone destruction reported by *López-Puertas et al.* [2005a].

4.2. Antarctic HOCl and ClO Enhancements

[17] The response of the southern polar stratosphere to the SPEs is much weaker compared with its northern counterpart [*López-Puertas et al.*, 2005a, 2005b]. This also holds for the SPE-induced HOCl formation, whose amplitude is about a factor of two smaller compared with the Arctic (Figure 4). The maximal response was observed at nighttime at 47 km altitude, while HOCl enhancement in the sunlit Antarctic stratosphere was less pronounced by a factor of 6 and peaked at 38 km altitude (not shown here because it is not clear if significant). Similar as for the Arctic, the response to the SPE on 29 October is by far the strongest, which is in agreement with the modeled OH signal at these altitudes [*Jackman et al.*, 2005]. The apparent enhancements on 7 and 11 November in the Antarctic again are explained as a sampling artefact. The HOCl decay happened to be much faster compared with the northern polar region (half value period of several hours), which can be explained through reactions R4 and R7 by longer illumination of the HOCl-rich area.

[18] The most prominent Antarctic HOCl enhancement occurred in subpolar latitudes around 60°S, at geomagnetic

high latitudes (Figure 5, middle) approximately where largest HOCl abundances were measured on 29 October. At the area of largest HOCl, only nighttime MIPAS measurements were available for the solar storm period. Therefore it is not possible to judge from MIPAS data alone, if the spatial distribution of the measured HOCl abundances is dominated by geomagnetic or diurnal effects.

[19] The largest ClO signal is seen at 35 km altitude and, in contrast to the northern polar region, the ClO response is delayed by 2 days. Immediately after the SPE, even ClO reduction was observed. The delayed ClO increase is assigned to HOCl decomposition via R7 or R4. However, the spatial distribution of ClO in the southern polar stratosphere lacks clear structures, and sampling artefacts may play a more important role here compared with the Northern Hemisphere. Larger natural scatter of the data within the sample and smaller mixing ratios result in less significant time series. No clear signal is seen in the $ClONO_2$ temporal development, and $ClONO_2$ mixing ratios were only around 0.02 ppbv at 44 km altitude. The center of the southern polar ozone minimum is shifted toward higher geomagnetic latitudes but this is no unambiguous hint at a predominant role of odd hydrogen chemistry in this altitude because all other SPE-induced chemistry is assumed to happen there, too. (Figure 5, bottom).

5. Summary and Conclusion

[20] The rapid increase of HOCl at 32 to 52 km altitude in the Arctic polar atmosphere on 29 October 2003 gives clear evidence of enhanced odd hydrogen abundances related to the solar proton event. This is confirmed by a strong increase of ClO at 28 to 60 km. The solar proton events on 2 and 4 November caused much smaller ClO and HOCl responses, presumably since much less HO_x was available then. When HOCl disappeared, $ClONO_2$ amounts increased. This indicates, that OH chemistry has shifted the chlorine reservoir partitioning from HCl toward $ClONO_2$. Spatial anticorrelation of ClO and HOCl suggests that reduced ClO availability due to buffering of ClO into $ClONO_2$ might not have been an obstacle to persistent HOCl formation, when $ClONO_2$ was observed to increase. Instead, HOCl abundances seem to be rather driven by odd hydrogen chemistry. MIPAS measurements are consistent with the assumption that ozone reduction after 29 October is caused at least in part by the OH catalytic cycle triggered by the SPEs, as suggested by *Jackman and McPeters*, [2004] and *Jackman et al.* [1995]. However, these measurements suggest that ozone loss in the middle to upper stratosphere after the SPE can also be driven by enhanced ClO_x and ClO_x–HO_x cycles. The SPE-induced HOCl signal observed in the Southern Hemisphere is much weaker, extends wider to subpolar latitudes, shows a strong diurnal dependence (nighttime enhancement), and is collocated with a region where unfortunately no MIPAS daytime data are available. This adds difficulty to the judgement if the distribution is dominated by diurnal or regional effects. An unexplained delay of Antarctic ClO enhancement is observed. Further insight is expected from model calculations.

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